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Exact Partition Functions for the Primitive Droplet Nucleation Model in 2 and 3 Dimensions

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Abstract

The grand canonical partition functions for primitive droplet nucleation models with an excess energy $\epsilon_n = -\hat{\mu}\, n + \sigma\, n^{1-\eta}, \eta = 1/d$, for droplets of n constituents in d dimensions are calculated exactly in closed form in the cases $d = 2$ and 3 for all (complex) $\hat{\mu}$ by exploiting the fact that the partition functions obey simple linear PDE.

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The picture that 1st-order phase transitions are initiated by the formation (homogeneous nucleation) of expanding droplets of the new phase within the old phase is a familiar and important one (see the reviews [1-13]). In its most primitive form the droplets are considered to consist of n constituents (e.g. droplets of Ising spins on a lattice or liquid droplets of molecules etc.), the "excess" energy ϵ_n of which is given by a "bulk" term proportional to n and a "surface" term proportional to $n^{1-\eta}, \eta = 1/d$, where $d \geq 2$ is the dimension of the system:

$$\epsilon_n = -\hat{\mu} n + \sigma n^{1-\eta} \ , \quad \eta = 1/d \ . \tag{1}$$

In the case of negative Ising spin droplets formed in a background of positive spins by turning an external magnetic field H slowly negative, below the critical temperature, the coefficient $\hat{\mu}$ in Eq. (1) takes the form $\hat{\mu} = -2H$. For liquid droplets of n molecules condensing from a supersaturated vapour one has $\hat{\mu} = \mu - \mu_c$, where μ is the chemical potential and μ_c its critical value at condensation point.
Assuming the average number $\bar{\nu}(n)$ of droplets with n elements to be given by a Boltzmann factor,

$$\bar{\nu}(n) \propto e^{-\beta\epsilon_n} \ , \ \beta = \frac{1}{k_B T} \ , \tag{2}$$

and that the droplets form a noninteracting dilute gas leads to the grand canonical potential ψ_d per spin or per volume

$$\begin{aligned} \psi_d(\beta, t = \beta\hat{\mu}) &= \ln Z_G = p\beta = \sum_{n=0}^{\infty} e^{tn - xn^{1-\eta}} \ , & (3) \\ & t = \beta\hat{\mu}, \ x = \beta\sigma \ ; \ p : \text{pressure} \ , & \\ & d\psi_d = -U d\beta + \bar{n} dt \ . & (4) \end{aligned}$$

(Physical reasons may require to start the sum (3) not at $n = 0$ but at some finite $n_0 > 0$. This does not affect the following conclusions and can easily be taken care of. It is mathematically convenient to start at $n = 0$.)
The series (3) converges for $t \leq 0$ only, which follows e.g. from the Maclaurin-Cauchy integral criterium [14]. In applications to metastable systems one is interested, however, in the behaviour of $\psi_d(t, x)$ for $t \geq 0$ which calls for an analytic continuation in t or in the fugacity $z = e^t$ [15, 16, 17].
The series (3) has recently been discussed in connection with the canonical

quantum statistics of Schwarzschild black holes [18, 19, 20].
Notice that it obeys the linear PDE

$$\partial_t^{d-1}\psi_d = (-1)^d\,\partial_x^d\psi_d \quad , \tag{5}$$

in particular

$$\begin{aligned} \partial_t\psi_2 &= \partial_x^2\psi_2 \quad \text{for } d=2 \ , & (6)\\ \partial_t^2\psi_3 &= -\partial_x^3\psi_3 \ \text{ for } d=3 \ , & (7) \end{aligned}$$

which will be helpful to find ψ_d for $t \geq 0$, in the following especially for $d = 3$. Before discussing the exact continuation of ψ_2 and ψ_3 into the complex t- or z-plane, let me recall the known saddle point approximations for ψ_d if n is turned into a continuous variable and $t > 0$ [16, 5]:

$$\tilde{\psi}_d = \int_0^\infty dn\, e^{\beta(\hat{\mu}\, n - \sigma\, n^{1-\eta})} \quad . \tag{8}$$

Setting $n = (\sigma/\hat{\mu})^d u^d$ yields

$$\tilde{\psi}_d = d\left(\frac{\sigma}{\hat{\mu}}\right)^d \int_0^\infty du\, u^{d-1} e^{\beta h(u)} \ ,\ h(u) = a(u^d - u^{d-1}) \ ,\ a = \frac{\sigma^d}{\hat{\mu}^{d-1}} \ . \tag{9}$$

The function $h(u)$ has extrema at $u = u_0 = 0$ and at $u = u_1 = 1 - \eta$ with $h(u_1) = -a\eta(1-\eta)^{d-1}$, $h''(u_1) = a(d-1)(1-\eta)^{d-3}$. According to the standard analysis [21] the integral (9) has for large β the asymptotic expansion

$$\tilde{\psi}_d \sim (1-\eta)^{d/2}\sqrt{\frac{\pi\, d}{2\beta\,\hat{\mu}}}\left(\frac{\sigma}{\hat{\mu}}\right)^{d/2} e^{-\beta a\eta(1-\eta)^{d-1}}(i + O(1/\beta)) \ . \tag{10}$$

Here the path in the complex u-plane goes from $u_0 = 0$ to u_1 and then parallel to the imaginary axis to $+i\infty$. Thus, only half of the associated Gaussian integral along the steepest descents contributes! The leading terms in (10) are purely imaginary! For $d = 2$ and 3 (here see also Ref. [16]) one has

$$\begin{aligned} \tilde{\psi}_2^{(\infty)}(t,x) &= i\frac{\sqrt{\pi}x}{2t^{3/2}}e^{-x^2/(4t)} \ , & (11)\\ \tilde{\psi}_3^{(\infty)}(t,x) &= i\frac{2\sqrt{\pi}x^{3/2}}{3t^2}e^{-\dfrac{4}{27}\dfrac{x^3}{t^2}} \ . & (12) \end{aligned}$$

Whereas $\tilde{\psi}_2^{(\infty)}$ is a solution of the heat equation (6), $\tilde{\psi}_3^{(\infty)}$ is not an exact solution of the corresponding equation (7)! We shall see below how this is to be understood in terms of the exact $\psi_3(t,x)$.
For $d=2$ the function $\psi_2(t,x)$ has been determined exactly for $t>0$ in closed form in Ref. [18] by following Lerch's observation [22] that the relation

$$\begin{aligned} e^{-\sqrt{nx^2}} &= \frac{|x|}{\sqrt{\pi}}\int_0^\infty dv e^{-x^2v^2/4 - n/v^2} \\ &= \frac{|x|}{2\sqrt{\pi}}\int_0^\infty \frac{d\tau}{\tau^{3/2}} e^{-x^2/(4\tau) - n\tau} =: \int_0^\infty d\tau \hat{K}(\tau,x) e^{-n\tau} \end{aligned} \tag{13}$$

converts the series(3) into a geometrical one under the integral sign. Here

$$\hat{K}(t,x) = \frac{x}{2\sqrt{\pi t^3}} e^{-x^2/(4t)} = -2\partial_x K(t,x) \ , \tag{14}$$

where

$$K(t,x) = \frac{1}{\sqrt{4\pi t}} e^{-x^2/(4t)} \tag{15}$$

is the "heat kernel" which obeys the heat equation (6). So does $\hat{K}(t,x)$.
Now the series (3) can be summed exactly for $t<0$ ($x>0$) and then continued:

$$\psi_2(z=e^t,x) = \int_0^\infty d\tau \hat{K}(\tau,x) \frac{1}{1-e^{(t-\tau)}} \tag{16}$$

$$= \frac{x}{2\sqrt{\pi}} \int_1^\infty du \, \frac{e^{-x^2/(4\ln u)}}{\ln^{3/2} u} \frac{1}{u-z} \quad . \tag{17}$$

The last relation shows that $\psi_2(z,x)$ can be continued analytically into the whole complex z-plane except for a cut from $z=1$ to $z=\infty$.
The discontinuity of ψ_2 across the cut (z real and >1) is given by

$$\lim_{\epsilon\to 0^+} [\psi_2(z+i\epsilon) - \psi_2(z-i\epsilon)] = 2\pi i \hat{K}(t,x) \ , \tag{18}$$

and, if one approaches the cut from above, the limit

$$\lim_{\epsilon\to 0^+} \psi_2(z+i\epsilon,x), \ z \text{ real and } >1 \ ,$$

is no longer a real-valued function of z, but has a nonvanishing imaginary part

$$\Im[\psi_2(t,x)] = \pi\hat{K}(t,x) = \frac{\sqrt{\pi}x}{2t^{3/2}}e^{-x^2/(4t)} \quad , \tag{19}$$

which agrees exactly with that of the saddle point approximation (11)!
The real part $\Re[\psi_2(t,x)]$ is given by the principal value integral

$$\Re[\psi_2(t,x)] = \text{p.v.} \int_0^\infty d\tau\, \hat{K}(\tau,x)\frac{1}{1-e^{t-\tau}} \ . \tag{20}$$

In order to prepare for the method by which to determine ψ_3, let us arrive at the above result for ψ_2 in a different way:
As the heat equation (6) is invariant under the scale transformation $t \to \lambda t, x \to \lambda^2 x, \lambda > 0$, it has solutions of the type $g(y = x^2/t)$, where $g(y)$ obeys the ODE

$$g'' + (\frac{1}{4} + \frac{1}{2y})g' = 0 \ . \tag{21}$$

The solutions (up to additive and multiplicative constants) are (see Ref. [23])

$$g(y) = y^{-1/4}e^{-y/8}w(k = -1/4, m = 1/4; y/4) \ , \tag{22}$$

where w is any solution of Whittaker's standard form of the confluent hypergeometric equation [24]. As we want to associate the solution g with the imaginary part $\Im[\psi_2]$ in (11), we take $w(-1/4, 1/4; y/4) = aW_{-\frac{1}{4},\frac{1}{4}}(y/4), a$: constant, where $W_{k,m}$ is Whittaker's "W"-function which has the property [24]

$$u^{-1/2}e^{-1/2u^2}W_{-\frac{1}{4},\frac{1}{4}}(u^2) = 2\int_u^\infty dve^{-v^2} \equiv 2\text{Erfc}(u). \tag{23}$$

Here Erfc(u) is the complementary error function. Thus we get

$$g(y) = \text{const. Erfc}(\frac{1}{2}\sqrt{y}) \ . \tag{24}$$

As

$$\partial_t \text{Erfc}(\frac{1}{2}\sqrt{y}) = \frac{x}{4t^{3/2}}e^{-x^2/(4t)} = \frac{\sqrt{\pi}}{2}\hat{K}(t,x) \ , \tag{25}$$

we see that we may arrive at the solution (16) by essentially folding the imaginary part $\partial_t g(y)$ with the function $1/(1-e^{t-\tau})$. (Note: If $F(t,x)$ is a

solution of the heat equation, then any derivative or integral of $F(t,x)$ with respect to t or x is a solution, too!)
The normalization of $g(y)$ is fixed by observing that for $\lambda > 0$ we have (by rescaling $\tau \to \lambda^2\tau$)

$$\psi_2(t,\lambda x) = \int_0^\infty d\tau \hat{K}(\tau,x) \frac{1}{1-\exp(t-\lambda^2\tau)} \ , \tag{26}$$

and that therefore

$$\lim_{\lambda\to 0} \psi_2(t,\lambda x) = \frac{1}{1-e^t} \ , \quad \lim_{\lambda\to\infty} \psi_2(t,\lambda x) = 1 \ . \tag{27}$$

We are now ready to proceed in the same way for ψ_3: As the PDE (7) is invariant under the scaling [19] $t \to \lambda t, x \to \lambda^{2/3}x$, the ansatz $g(y = x^3/t^2)$ leads to the ODE

$$g''' + (\frac{4}{27} + \frac{2}{y})g'' + \frac{2}{9}(\frac{1}{y} + \frac{1}{y^2})g' = 0 \ , \tag{28}$$

which has solutions (see Ref. [23])

$$g'(y) = y^{-1} e^{-\frac{2}{27}y} w(1/2, 1/6; \frac{4}{27}y) \ . \tag{29}$$

The choice $w = W_{\frac{1}{2},\frac{1}{6}}(\frac{4}{27}y)$ provides the desired result:
With

$$g(y) = \int_y^\infty \frac{d\eta}{\eta} e^{-\frac{2}{27}\eta} W_{\frac{1}{2},\frac{1}{6}}(\frac{4}{27}\eta) \tag{30}$$

we have

$$\partial_t g(y) = \frac{2}{t} e^{-\frac{2}{27}y} W_{\frac{1}{2},\frac{1}{6}}(\frac{4}{27}y) \ , \tag{31}$$

which for large y, i.e. large x or small t, takes the asymptotic form [24]

$$\partial_t g(y) \sim \frac{4}{(\sqrt{3})^3} \frac{x^{2/3}}{t^2} e^{-\frac{4}{27}x^3/t^2} \ . \tag{32}$$

Except for a factor $\sqrt{3\pi}/2$ this is the same as $\tilde{\psi}_3^{(\infty)}$ in Eq. (12).
Let us, therefore, try the ansatz

$$\psi_3(t,x) = \int_0^\infty d\tau \hat{K}_3(\tau,x) \frac{1}{1-e^{t-\tau}} \ , \tag{33}$$
$$\hat{K}_3(\tau,x) = \alpha \, \frac{1}{\tau} e^{-\frac{2}{27}x^3/\tau^2} W_{\frac{1}{2},\frac{1}{6}}(\frac{4}{27}x^3/\tau^2) \ \ ,$$

where α is a normalization constant to be determined.
That the function ψ_3 of Eq. (33) is indeed the right one can be seen as follows: It is a solution of Eq. (7), because by construction $\hat{K}_3(t,x)$ is a solution of that equation (the partial derivative of ψ_3 with respect to t can be replaced under the integral by the negative derivative with respect to τ, followed by a partial integration with repect to τ and observing that $\hat{K}_3$ vanishes at the boundaries, see Eqs. (32) and (39)).
Furthermore, the imaginary part of ψ_3 coincides with that of Eq. (12). Finally, the required boundary conditions can be fulfilled by an appropriate choice of α:
Rescaling $\tau \to \lambda^{3/2}\tau$ yields

$$\psi_3(t,\lambda x) = \int_0^\infty d\tau \hat{K}_3(\tau,x) \frac{1}{1-\exp(t-\lambda^{2/3}\tau)} \ . \tag{34}$$

In order to have (see Eq. (3))

$$\lim_{\lambda\to 0} \psi_3(t,\lambda x) = \frac{1}{1-e^t} \ , \quad \lim_{\lambda\to\infty} \psi_3(t,\lambda x) = 1 \ , \tag{35}$$

we need

$$\int_0^\infty d\tau \hat{K}_3(\tau,x) = 1 \ . \tag{36}$$

Because the relation

$$\int_0^\infty \frac{du}{u} e^{-u} W_{\frac{1}{2},\frac{1}{6}}(2u) = \frac{\sqrt{\pi}}{\cos(\pi/6)} = 2\sqrt{\frac{\pi}{3}} \tag{37}$$

holds [25], the normalization (36) requires $\alpha = \sqrt{3/\pi}$, so that finally

$$\hat{K}_3(\tau,x) = \sqrt{\frac{3}{\pi}} \, \frac{1}{\tau} e^{-\frac{2}{27}x^3/\tau^2} W_{\frac{1}{2},\frac{1}{6}}(\frac{4}{27}x^3/\tau^2) \ \ . \tag{38}$$

Let me add that $\hat{K}_3(t,x)$ has no zeros on the positive real τ-axis for $x > 0$ [24] and therefore is strictly positive there. Furthermore, for $u \to 0$ one has [24]

$$W_{\frac{1}{2},\frac{1}{6}}(u) \to \frac{\Gamma(1/3)}{\Gamma(1/6)} u^{1/3}(1+O(u)) + \frac{\Gamma(-1/3)}{\Gamma(-1/6)} u^{2/3}(1+O(u)) \ , \qquad (39)$$

which is of interest for the behaviour of $\hat{K}_3(t,x)$ in the limits $x \to 0$ or t$\to \infty$. One can check the result (38) by expanding the factor $1/(1-e^{(t-\tau)})$ in the integrand of (33) for $t < 0$ in a geometrical series and comparing the coefficient

$$f(x,n) = \sqrt{\frac{3}{\pi}} \int_0^\infty d\tau \frac{1}{\tau} e^{-\frac{2}{27}x^3/\tau^2} \ W_{\frac{1}{2},\frac{1}{6}}(\frac{4}{27}x^3/\tau^2) \, e^{-n\,\tau} \qquad (40)$$

of $\exp(n\,t)$ with the one - $\exp(-x\,n^{2/3})$ - of the original series (3):
Because $f(\lambda x, n) = f(x, \lambda^{3/2} n)$, we have $f(x,n) = g(x\,n^{2/3})$ and it is sufficient to consider (40) for $x = 1$. $f(n) \equiv f(x=1,n)$ can be interpreted as the Laplace transform of

$$h(\tau^2) = \frac{1}{\sqrt{\tau^2}} e^{-\frac{2}{27\,\tau^2}} \ W_{\frac{1}{2},\frac{1}{6}}(\frac{4}{27\,\tau^2}) \ , \quad f(n) = \int_0^\infty d\tau e^{-n\,\tau} h(\tau^2) \ . \qquad (41)$$

In that case one has (see Ref. [26])

$$f(n) = \frac{1}{\sqrt{\pi}} \int_0^\infty \frac{du}{u^2} e^{-n^2\,u^2/4} g(1/u^2) \ , \qquad (42)$$

where $g(y)$ is the Laplace transform of $h(t = \tau^2)$.
As [27]

$$g(y) = \int_0^\infty dt e^{-y\,t} h(t) = \frac{4}{\sqrt{27}} K_{1/3}(4\sqrt{\frac{y}{27}}) \ \ , \qquad (43)$$

where $K_\nu(z)$ is the modified Hankel function [28], we finally get from Eqs. (42) and (43) the desired result (compare Ref. [29]):

$$f(n) = \frac{1}{3\pi} \int_0^\infty \frac{dv}{v^{3/2}} e^{-n^2\,v} K_{1/3}(\frac{2}{\sqrt{27\,v}}) = e^{-n^{2/3}} \ . \qquad (44)$$

As (see Ref. [30])

$$W_{\frac{1}{2},\frac{1}{6}}(2z) = \frac{\sqrt{2z}}{2}(W_{0,\frac{1}{3}}(2z) + W_{0,\frac{2}{3}}(2z)) = \frac{z}{\sqrt{\pi}}(K_{\frac{1}{3}}(z) + K_{\frac{2}{3}}(z)) \ , \qquad (45)$$

$\hat{K}_3(\tau, x)$ may also be expressed by these special functions.
Having determined the exact partition functions, one can now study the associated thermodynamical properties, e.g. the behaviour of the magnetization which is essentially given by the derivative of ψ_d with respect to t, the details of the metastabilities etc. However, improving the mathematics does not eliminate the many shortcomings of the model concerning the physics it is supposed to approximate (see the Refs. [1-13])! Nevertheless, it is always pleasing to have exact solutions for nontrivial models.

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